LETTERS TO THE EDITOR

The Letters to the Editor section is divided into three categories entitled Notes, Comments, and Errata. Letters to the Editor are limited to one and three-fourths journal pages as described in the Announcement in the 1 January 2000 issue.

COMMENTS

Comment on "Positron and positronium chemistry by quantum Monte Carlo. IV. Can this method accurately compute observables beyond energy" [J. Chem. Phys. 111, 108 (1999)][a)]

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In a recent series of papers Bressanini and co-workers[1–4] have used the quantum Monte Carlo (QMC) method to investigate positron and positronium (Ps) binding to a number of atoms and molecules. They have also demonstrated that the QMC[4] can be used to accurately calculate annihilation rates and reproduced annihilation rates computed using variational techniques.[5]

Their calculated annihilation rate for [LiH, e^+] was 1.2×10^9 s^{-1}, a number that was significantly smaller than the annihilation rates they attained for PsH, Lie^+, and LiPs. In their article, Mella, Morosi, and Bressanini[4] stated *differently to what happens in the other* [atomic] *systems, the positron distribution is no longer isotropic around the H nucleus, but strongly polarized outward* [in] *the bound region due to the repulsive interaction with the Li nucleus. This repulsion decreases the overlap between the electronic and positronic distributions, reducing in this way the probability of an annihilative collision.* One limitation to this explanation was the lack of quantitative information, there was no way of deciding whether the rate should be reduced to 1.5 or 0.2×10^9 s^{-1}.

However, there is an alternate explanation for the smaller [LiH,e^+] annihilation rate which can also be used to give a rough estimate of the expected annihilation rate. It has recently been suggested[6,7] that the structure of any positronic atom or ion can heuristically be written as

$$\Psi = \alpha\Phi(\text{atom})\phi(e^+) + \beta\Omega(\text{atom}^+)\omega(\text{Ps}). \quad (1)$$

The first of these terms represents a positron moving in the field of a polarized atom while the second term represents a Ps cluster attached to the residual ion (or atom). The relative strength of these two configurations is determined by the ionization potential (or electron affinity) of the atomic (or ionic) parent. When the ionization potential is less than 6.8 eV (the positronium binding energy) the most loosely bound electron is attached to the positron forming a positronium cluster. However, when the ionization potential is greater than 6.8 eV, the tendency to form a Ps cluster is disrupted by the stronger attraction of the electron to the parent atom. This heuristic model of the structure is consistent with all the available evidence.

Electron–positron correlation functions (i.e., the probability of finding the electrons and positron a certain distance apart) for Lie^+, Nae^+, Cue^+, Age^+, and He($^3S^e$)e^+ look increasingly similar to the (ground state) Ps correlation function as the ionization potential of the parent atom decreases.[6] This tendency for the electron–positron probability distribution to increasingly resemble the Ps probability distribution as the ionization potential decreases was also apparent in an investigation of positron binding to a model alkali atom.[7] Correlation functions and expectation values for the alkali–Ps ground states[8] (i.e., LiPs, NaPs, and KPs) are also consistent with the model. The electron-affinities for the alkali–Ps systems are all much smaller than the Ps binding energy and therefore these systems can be expected to have a well-defined Ps cluster.

Positron annihilation data also support the heuristic model. The spin-averaged annihilation rates for a number of positron binding systems are shown in Fig. 1. The horizontal axis measures the binding energy of the last electron to the parent system, i.e., the ionization potential for Lie^+ and the electron affinity for LiPs. There is a tendency for systems with small ionization potentials (or electron affinities) to have an annihilation rate close to 2×10^9 s^{-1} (the Ps annihilation rate). The situation for two valence electron systems is complicated by the fact that cluster annihilation (the annihilation with the electron forming the Ps cluster) or pick-off annihilation (the annihilation with the rest of the electrons) can contribute to the annihilation rate. The annihilation rates for the alkali–Ps systems,[5,8] are all close to 2×10^9 s^{-1} and therefore consistent with a well-defined Ps cluster. The closeness of the annihilation rate to 2×10^9 s^{-1} implies that the pick-off annihilation is relatively small. The PsH system is the only system to have an annihilation rate (per positron)

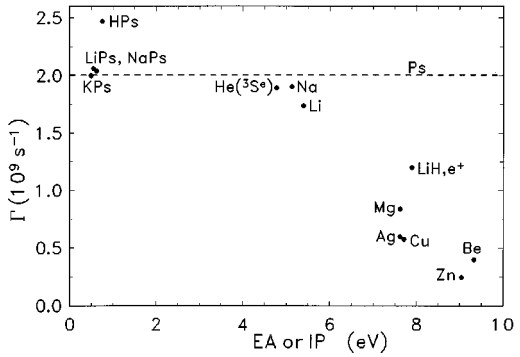

FIG. 1. The spin-averaged annihilation rate (in units of 10^9 s^{-1}) vs ionization potential or electron affinity (in electron volts) for a number of positron binding systems.

much larger than 2×10^9 s^{-1}. The larger annihilation rate is a consequence of the compact size of the system (the mean positron–proton distance for PsH[5] is 3.5 a_0) which is smaller than most alkali atoms.

The annihilation rate for the $[LiH,e^+]$ system was plotted in Fig. 1 after deriving an ionization potential of 7.9 eV from the potential curves of Gianturco[9] at an internuclear distance of 3.0 a_0. Mella, Morosi, and Bressanini[4] were concerned about the small size of the annihilation rate. However, the $[LiH,e^+]$ data point is consistent with the established trend for atomic systems although the annihilation rate is somewhat larger than the rate for Mge^+ which has a similar ionization potential. Detailed numerical agreement with the annihilation rate data obtained for atomic systems should not be expected as the distinctly different electron distributions for molecules can be expected to have some influence on the annihilation rate. Nevertheless, the conceptual model does give a reasonable first estimate of the annihilation rate.

The $[LiH,e^+]$ system is the only positron binding molecular system for which an annihilation rate yet has been computed. The recent extension of QMC method to compute annihilation rates[4,10] should permit the investigation of other positron binding systems and thereby support or refute the conceptual model described in this comment. One simple test would be to compute the annihilation rate as a function of internuclear distance (R). The vertical ionization potential for LiH decreases as R increases,[9] and therefore the conceptual model suggests the annihilation rate should increase as R increases.

[a]The Response to this Comment can be found in the 22 February 2000 issue of *The Journal of Chemical Physics*, Vol. 112, No. 8, pp. 3928–3929.
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